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	5c. PROGRAM ELEMENT NUMBER 0D10BD
6. AUTHORS Evelyn L. Hu, David Awschalom, David R. Clarke, Roger Hanlon, David Mooney, Kevin Kit Parker, Zhigang Suo	5d. PROJECT NUMBER
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14. ABSTRACT

This final report describes the research activities of the Center for Cephalopod-INspired Adaptive Photonic SystEms (CINAPSE). CINAPSE comprises a distinctive group of researchers with broad expertise in cephalopod coloration and behavior, the physics, mechanics and applications of elastomeric materials, the use of tissue engineering to form engineered devices, the synthesis, characterization and utilization of inorganic materials into optical devices, as well as experts in the optical characterization of materials. Advances made through the course of

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Report Title

Cephalopod-INspired Adaptive Photonic SystEms (CINAPSE)

ABSTRACT

This final report describes the research activities of the Center for Cephalopod-INspired Adaptive Photonic SystEms (CINAPSE). CINAPSE comprises a distinctive group of researchers with broad expertise in cephalopod coloration and behavior, the physics, mechanics and applications of elastomeric materials, the use of tissue engineering to form engineered devices, the synthesis, characterization and utilization of inorganic materials into optical devices, as well as experts in the optical characterization of materials. Advances made through the course of the program included new insights into the structure and mechanism of cephalopod coloration, exceptional elastomeric behavior, new insights into the microstructure and optical performance of cephalopod coloration, and new means of coloration display in gels and polymeric materials.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
08/13/2013	7.00	Jiangshui Huang, Tongqing Lu, Jian Zhu, David R. Clarke, Zhigang Suo. Large, uni-directional actuation in dielectric elastomers achieved by fiber stiffening, Applied Physics Letters, (05 2012): 2119011. doi: 10.1063/1.4720181
08/13/2013	8.00	Tongqing Lu, Jiangshui Huang, Christa Jordi, Gabor Kovacs, Rui Huang, David R. Clarke, Zhigang Suo. Dielectric elastomer actuators under equal-biaxial forces, uniaxial forces, and uniaxial constraint of stiff fibers, Soft Matter, (04 2012): 6167. doi: 10.1039/c2sm25692d
08/13/2013	9.00	Harold S. Park, Zhigang Suo, Jinxiong Zhou, Patrick A. Klein. A dynamic finite element method for inhomogeneous deformation and electromechanical instability of dielectric elastomer transducers, International Journal of Solids and Structures, (08 2012): 2187. doi: 10.1016/j.ijsolstr.2012.04.031
08/13/2013	10.00	Matthias Kollosche, Jian Zhu, Zhigang Suo, Guggi Kofod. Complex interplay of nonlinear processes in dielectric elastomers, Physical Review E, (05 2012): 518011. doi: 10.1103/PhysRevE.85.051801
08/13/2013	11.00	Tiefeng Li, Christoph Keplinger, Richard Baumgartner, Siegfried Bauer, Wei Yang, Zhigang Suo. Giant voltage-induced deformation in dielectric elastomers near the verge of snap-through instability, Journal of the Mechanics and Physics of Solids, (02 2013): 611. doi: 10.1016/j.jmps.2012.09.006
08/13/2013	12.00	Jeong-Yun Sun, Xuanhe Zhao, Widusha R. K. Illeperuma, Ovijit Chaudhuri, Kyu Hwan Oh, David J. Mooney, Joost J. Vlassak, Zhigang Suo. Highly stretchable and tough hydrogels, Nature, (09 2012): 133. doi: 10.1038/nature11409
08/13/2013	13.00	Tong-Qing Lu, Zhi-Gang Suo. Large conversion of energy in dielectric elastomers by electromechanical phase transition, Acta Mechanica Sinica, (09 2012): 1106. doi: 10.1007/s10409-012-0091-x
08/13/2013	14.00	Jian Zhu, Matthias Kollosche, Tongqing Lu, Guggi Kofod, Zhigang Suo. Two types of transitions to wrinkles in dielectric elastomers, Soft Matter, (06 2012): 8840. doi: 10.1039/c2sm26034d
08/28/2013	15.00	E. Kreit, L. M. Mathger, R. T. Hanlon, P. B. Dennis, R. R. Naik, E. Forsythe, J. Heikenfeld. Biological versus electronic adaptive coloration: how can one inform the other?, Journal of the Royal Society Interface, (09 2012): 1. doi: 10.1098/rsif.2012.0601
08/28/2013	16.00	George R.R. Bell, Alan M. Kuzirian, Stephen L. Senft, Lydia M. Mäthger, Trevor J. Wardill, Roger T. Hanlon. Chromatophore radial muscle fibers anchor in flexible squid skin, Invertebrae Biology, (06 2013): 120. doi: 10.1111/ivb.12016
08/28/2013	19.00	L. M. Mathger, G. R. R. Bell, A. M. Kuzirian, J. J. Allen, R. T. Hanlon. How does the blue-ringed octopus (Hapalochlaena lunulata) flash its blue rings?, Journal of Experimental Biology, (10 2012): 3752. doi: 10.1242/jeb.076869
08/28/2013	20.00	T. J. Wardill, P. T. Gonzalez-Bellido, R. J. Crook, R. T. Hanlon. Neural control of tuneable skin iridescence in squid, Proceedings of the Royal Society B: Biological Sciences, (08 2012): 4243. doi: 10.1098/rspb.2012.1374
TOTAL:	**12**	

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

1. Mooney, ‘Materials to program cells in situ’, American Chemical Society National Meeting, Aug. 22-26, 2010
2. Mooney, ‘Active Scaffolds for On-demand Drug and Cell Delivery’, Science Engineering Society Meeting at Iowa State University, Oct. 10, 2010
3. Mooney, ‘Polymeric systems for drug and cell delivery’, 11th Annual Wound Healing Symposium: Science and Industry, Dec. 8-11, 2010
4. Mooney, ‘Moving the biology in vivo’, 15th International Symposium Recent Advances Drug Delivery Systems, Feb. 13-16, 2011
5. Mooney, ‘Polymers to control cell trafficking’, Seminar: Tufts University Biomedical Engineering Dept., March 15, 2011
6. A.M. Kuzirian, ‘Histology and Physiology of Cephalopod Camouflage Elements: Form and Function being Revealed’, Anatomy & Physiology-II lecture. Cape Cod Community College, W. Barnstable, MA. January 25, 2011.
7. R.T. Hanlon, ‘Rapid adaptive camouflage and signaling by cephalopods: III Changeable skin. Controlling pigments and reflectors & implications for biotechnology.’ iBioSeminars on Web. Jul 2011.
8. R.T. Hanlon, ‘Camouflage mechanisms and functions: convergence of biology and optical physics’ SOCOM/U.S. Army National Ground Intel. Center, 16 May 2011
9. R.T. Hanlon, Bio-inspired adaptive coloration of nanomaterials: dynamics of neurally controlled skin patterning in cephalopods Kavli Institute of Bionanoscience and Technology, Plenary talk, 19 May 2011
10. R.T. Hanlon,’Visual control of dynamic camouflage in cephalopods’, Brown Univ., 14 Mar 2011
11. R.T. Hanlon, ‘Optical magic: nature’s best camouflage system and the confluence of art and science’, Rhode Island School of Design, 1 Mar 2011
12. R.T. Hanlon, ‘Color change and patterning in the ocean: science, art & technology, MBL, Woods Hole, MA 8 Feb 2011
13. R.T. Hanlon, ‘Optical malleability: light diffusers and dynamic 3-D skin texture in cephalopod skin’ AFOSR Annual Science Meeting, Washington, DC 8 Jan. 2011.
14. R.T. Hanlon, ‘Optical magic: how cephalopods sense and manipulate light to produce rapid adaptive camouflage and communication’, Ocean Optics Annual Meeting, Anchorage AK 27 Sep 2010
15. Deravi LF, Parker KK, ‘Molecular Changes in Protein nanoFabrics,’ Materials Research Society, Nov. 29- Dec. 3, 2010.
16. Zhigang Suo, November 28, 2010, “Large deformation and instability in swelling gels.” Symposium V Harnessing Instability in Soft Material Films and Interfaces. MRS Fall Meeting, Boston. Invited talk.
17. Zhigang Suo, November 16, 2010, “Theories and experiments on the mechanical behavior of polymeric gels.” Keynote. Symposium on the Mechanics of Soft Materials. ASME Winter Annual Meeting, Vancouver.
18. Zhigang Suo, June 29, 2010. “Mechanics and materials of soft machines”. Plenary lecture. U.S. National Congress on Theoretical and Applied Mechanics.

Number of Presentations: 18.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

11/28/2011 1.00 Xuanhe Zhao, Jaeyun Kimb, Christine A. Cezarb, Nathaniel Huebsch, Kangwon Leeb, Kamal Bouhadird, David J. Mooney. Active scaffolds for on-demand drug and cell delivery, Proceedings of the National Academy of Sciences (11 2010)

11/28/2011 2.00 Zhigang Suo. Theory of dielectric elastomers, Acta Mechanica Sinica (11 2010)

11/28/2011 3.00 J. Huang, J. Liu, B. Kroll, K. Bertoldi, D. R. Clarke. Spontaneous and Deterministic Three-dimensional Curling of Pre-strained Elastomeric Strips, Physical Review Letters (submitted) (09 2011)

11/28/2011 4.00 Jiangshui Huang, Tiefeng Li, Choon Chiang Foo, Jian Zhu, David R. Clarke, Zhigang Suo. Giant, voltage-actuated deformation of a dielectric elastomer under dead load, Soft Matter (11 2011)

TOTAL: 4

Number of Manuscripts:

Books

Received Paper

TOTAL:

Patents Submitted

Pixel Device and Display Using Liquid Ink and Elastomers
International Application No. PCT/US2013/022619
Samuel Shian, David Clarke and Roger Diebold

Pigment Structures, Pigment Granules, Pigment Proteins and Uses Thereof
Prov. Application U.S. 61/526,351
Leila Deravi, Kevin Kit Parker, Andrew Magyar, Evelyn Hu

Patents Awarded

Awards

David Awschalom: David Turnbull Award, Materials Research Society (2010), election to National Academy of Engineering (NAE) (2011)
David Mooney: election to NAE (2010)
Evelyn Hu: election to American Academy of Arts and Sciences (2010)

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Shanying Cui, Harvard	0.05	
Roger Diebold, UCSB	0.10	
Viva Horowitz, UCSB	1.00	
Joe Heremans, UCSB	0.25	
FTE Equivalent:	**1.40**	
Total Number:	**4**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Igor Aharonovich, Harvard	0.00
Andrew Magyar, Harvard	1.00
Lee Bassett, UCSB	0.25
Leila Deravi, Harvard	1.00
Jiangshui Huang, Harvard	1.00
Jayna Jones, UCSB	0.00
Stephen Kennedy	0.33
Kangwon Lee, Harvard	0.50
Samuel Shian, Harvard	0.50
Jian Shu, Harvard	0.00
FTE Equivalent:	**4.58**
Total Number:	**10**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
David Awschalom, UCSB-	0.08	Yes
David Clarke, Harvard	0.08	Yes
Evelyn Hu, Hrvard	0.08	Yes
Roger Hanlon, MBL	0.03	
Kit Parker, Harvard	0.08	
Zhigang Suo, Harvard	0.00	Yes
Alan Kuzirian, MBL	0.02	
Lydia Mathger, MBL	0.04	
FTE Equivalent:	**0.41**	
Total Number:	**8**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Seul (Kathy) Ku	0.00	
Alice Zhao (Harvard)	0.00	
Erzesebet Vincent (UCSB)	0.00	
FTE Equivalent:	**0.00**	
Total Number:	**3**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
Kuen Yong Lee, Harvard	1.00
Kurt Schellengberg, Harvard	0.04
Kimberly Ulmer, MBL	0.25
George Bell, MBL	0.11
Steve Senft, MBL	0.05
FTE Equivalent:	**1.45**
Total Number:	**5**

Sub Contractors (DD882)

Inventions (DD882)

5 **Pigment Structures, Pigment Granules, Pigment Proteins and Uses Thereof**

Patent Filed in US? (5d-1) N

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Leila Deravi, Kevin Kit Parker, Andrew Magyar, Evelyn Hu

5f-1a: Harvard University

5f-c: 29 Oxford Street

Cambridge MA 02138

5 **Pixel Device and Display Using Liquid Ink and Elastomers**

Patent Filed in US? (5d-1) N

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: Samuel Shian, David Clarke, Roger Diebold

5f-1a: Harvard University

5f-c: 29 Oxford Street

Cambridge MA 02138

Scientific Progress

We believe that the rapid, and broad-spectrum coloration change exhibited by cephalopods has distinctive advantages among the wide range of possible bio-inspired mechanisms. The interplay of color change exhibited by cephalopod chromatophores show an extraordinary increase in surface area (by a factor of 100), resulting in either 'color-on' states with structures that are on the order of millimeters (pixel-sized for many conventional, engineered displays) or 'color-off' states when the cross-sectional area of particular chromatophores are dramatically diminished. The collaborative effort of this program has allowed us to better understand the 'natural' structure that underlies the effectiveness of color tuning in cephalopods, and to incorporate those ideas into 3 integrative platforms that explore engineered versions of cephalopod-inspired rapid, tunable coloration change. All of these platforms have pushed the limits of performance in the materials utilized.

(a) Electro-active Hydrogel Arrays: One way of achieving dramatic changes in surface area that might emulate the rapid action demonstrated by cephalopod chromatophores is to employ macroporous materials such as hydrogels. Such materials are also amenable to the incorporation of various pigments to facilitate the demonstration of coloration change. An important focus is developing an electrical actuation scheme to collapse and restore the hydrogels. Major advances in this area include (1) achieving electrically collapsible polymeric hydrogels with response times 3 order of magnitude faster than previously reported. (2) achieving gel collapse to 10% of its original surface area and to 7% of its original volume, (3) the incorporation of pigments into the gel microstructure without compromising fast electrical responsivity, and (4) extending the range of operation of these hydrogel-based devices.

(b) Folded Structures: The 100x change in area observed for chromatophores in cephalopods implies a material strain that is beyond the simple capability of known elastomeric materials. Both the 'sac' of the chromatophore and the muscles that provide the actuation of the sac, must demonstrate exceptional strain. Research in this platform has created a series of elastomeric hetero-structures in which greater strain can be realized. A rich variety of complex, three dimensional shapes can be created from two-dimensional shapes by joining together a pre-strained elastomer to an unstrained elastomer, and then releasing them. The final shapes are fully deterministic, meaning that the same shape is produced each time, and they also exhibit non-linear but reversible strains when subsequently deformed. Many of these shapes are foldable, meaning that they automatically fold when released. 'Stiffened' elastomeric structures have been formed with a record 35% strain (compared to the standard 5%), with no lateral distortion. In addition, a novel coloration and signaling scheme has been developed (Soft Electroactive Polymer Ink displAY (SEPIA). It comprises an array of two-state systems in which circular areas on the surface of the device are either colored or clear, depending on the voltage applied to each element in the array. Each element in the array consists of a sac of colored ink held between two transparent membranes. Voltage-driven filling or removal of colored ink in the sac produces high-contrast color changes. In addition, work has progressed on forming transparent compliant electrodes for dielectric elastomers: critical for the electrical actuation of color-tunable devices utilizing dielectric elastomers.

(c) Bio-Photonic Protein Textiles: It is interesting to speculate about the possible unique optical properties of the pigment granules within the cephalopods, and whether those optical properties might provide some guidance for engineered approaches to coloration changed.

These thoughts provided the motivation for strongly collaborative research involving pigment isolation from Sepia (and also from Loligo), and some initial photoluminescence characterization of the pigments either dried, in solution, or incorporated into fibers or thin films.

Initial studies indicate a luminescence that may be emanating from some component of the pigment granules themselves, and interesting distinctions in fluorescence wavelengths according to pigment size and shape.

(d) Bio-Model Characterization: The close collaboration with researchers at the Marine Biological Laboratory has been invaluable, as have been the insights gained from a better understanding of the actual cephalopod structures and their relationship to coloration change. The advances made in understanding the nanostructure and microstructure of actual chromatophores provides critical input for the design of 'synthetic' chromatophores. In particular,

(1) The detailed microstructure of muscle attachment points for the actuation of chromatophores has guided the design of artificial muscles and the strains needed in those structures. Cephalopod chromatophores have a system of muscles that spatially separates the two functions of contraction and anchoring. Anchoring is accomplished by a system of extremely small and abundant anchor points between the muscles and surrounding connective tissue. Additionally, the muscle fiber branches multiple times at its terminus to form an arbor system. These arbors increase the surface area of the muscle, allowing for additional anchor points. Importantly, the system allows full expansion of the pigment cell without any significant distortion of the adjacent soft tissues.

(2) The elucidation of pigment tethers within the chromatophore sac allowed us to better understand potential issues of agglomeration and pigment density for engineered approaches. Color fidelity throughout all stages of expansion of the

chromatophore is extremely important for successful adaptive coloration. Cephalopod chromatophores solve this by the characteristics of pigments granules themselves and by a unique system used to distribute them evenly within the pigment cell. This latter characteristic is manifested in a network of fibrous tethers to which all the pigment granules are attached. As chromatophores are expanded, the pigments are essentially pulled into position in a non-random manner. This positional anchoring preserves a uniform pigment distribution devoid of any empty spaces, thus maintaining color fidelity. This design is newly discovered and may be reproducible using nanomaterials.

(3) Details of the size and distribution of pigments, keyed to the principal chromatophore colors (e.g., yellow, red, brown) will assist in constructing models of color modulation through dynamic absorption and reflection. squid and cuttlefish skin display different contrast differences, arising from the size and number of chromatophores per unit area. Squids have larger, less densely packed chromatophores arranged in specific patterns: typically a circle of smaller red and yellow chromatophores that surrounds a large brown chromatophore. Squid chromatophores can expand ~15x from their contracted (punctuate) state. Cuttlefish skin possesses smaller but more numerous and densely packed chromatophores arranged in a honeycomb lattice; each chromatophore expands only ~5x their punctate size. The two species represent separate arrangements that are analogous to high- and low-resolution displays.

(4) The availability of actual pigment granules for purification and characterization will help us better understand the intrinsic optical behavior of the chromatophores. Central to biological color displays is the nature of the pigments producing color. Using specifically developed isolation techniques, we learned how to separate either single-colored chromatophores or aliquots of individual color classes. Microscopic and morphometric analyses of chromatophore pigment granules revealed distinct size classes based upon color. There were also textural differences noted between the colored granules. We identified that granules exhibited a distinct fluorescent emission spectrum shift into the near-red wavelengths (610-630 ¿) when excited by a 514 ¿ (blue-green) laser beam. The luminescent emission intensity was coupled to pigment color, with yellow granules having the highest intensity followed by red then brown. Further studies of pigment granule structure and composition underlie an ingenious hierarchical structure where pigment granule composition, emission spectra and granule morphology are key features that enable light absorbance even when the pigment cell is maximally expanded and the path length is only a few pigments thick.

Technology Transfer